



Introduction of PFAS (Forever Chemicals) in Water

An Online Continuing Education Course for Engineers

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INTRODUCTION

Nothing lives forever except the moon and stars- and the bonds between carbon and fluorine...the two atoms vital to the creation of per- and polyfluoroalkyl molecules, aka PFAS- the forever chemicals. This course discusses the chemistry and science behind the development of PFAS, the harmful effects of these substances on the environment and human health, the role of the US Environmental Protection Agency (EPA) in protecting the citizens of the United States from health impacts associated with some of the PFAS chemicals, with special emphasis EPA's role related to drinking water protection.

The logic and science used by government agencies to set up risk assessment paradigms used for setting POFAS contaminant treatment limits are also reviewed. A brief overview of the Safe Drinking Water Act is presented with emphasis on EPA's strategic roadmap for PFAS control. Current PFAS wastewater treatment, removal and remediation methods are the final topics discussed.

A summary of the topics reviewed in the course is included in the closing chapter.

PFASs, otherwise known as Per- and polyfluoroalkyl substances, are a group of synthetic chemicals that include at least one fully fluorinated carbon molecule. Due to this unique molecular arrangement, very strong bonds develop between the atoms created, allowing for the production of many different combinations of PFAS-based products. PFAS products are extremely stable due to these CF bonds, and introducing them into other product productions allows for the manufacturing of different materials to repel oil, grease, water, and heat. These properties make them ideal for use in many different consumer, commercial, and industrial products, such as nonstick cookware (Teflon), shampoos, paints, cleaning products, and fire suppression systems.

The discovery of PFAS byproducts in drinking water, waste disposal sites, fire extinguishing foam, manufacturing facilities producing or using them, consumer products, food packaging, biosolids (sludge), and foods (fish and dairy) was the catalyst for EPA to research their effects on the environment and human health. This led to the development of new regulations for controlling the use, disposal, and treatment of specific PFAS compounds. The presence of certain PFAS compounds in drinking water and both surface- and ground-water sources is of increasing public concern due to their threat to human health, widespread use, and long-term environmental persistence.

The US Environmental Protection Agency (EPA) is the federal agency responsible for protecting the citizens of the United States from contaminants that are harmful to health and the environment. The EPA, as of October 2021, developed a *PFAS Strategic Roadmap* for restricting PFAS contamination; the scope of the roadmap includes providing research and monitoring programs, as well as naming remediation actions to prevent contamination of the nation's drinking waters. Actions to protect other areas of the environment from PFAS wastewater discharges, stormwater, and hazardous waste sites are also under investigation.

Later in this course, a discussion of PFAS effects on drinking water, the establishment of contaminant levels, PFAS treatment processes, and future additions to the list of pollutants regulated by the Safe Drinking Water Act is explained. Contaminants listed in the SDWA are assigned a maximum contaminant level (mg/l or ppm/ppt.) or maximum contaminant goal, and current methods for developing the proposed are also explored.

Two different regulatory tracks addressing PFAS are under development by EPA in partnership with other federal, state, non-profit, and other groups, to protect the environment and public health from PFAS.

- The first track *is to find and provide information on the sources for the various PFAS contaminants,*
- *The second one is to establish maximum containment levels and maximum containment goals in surface and drinking waters.*

Before any understanding of how PFAS chemicals come about, one must first start with a review of the basic chemical and atomic principles used to create carbon-fluorine molecules and how their unique atomic properties are responsible for their resistance to degradation and hydration. An understanding of their chemistry leads to an understanding of why the moniker "forever chemicals" is used to explain the impact of PFAS waste products on the public.

Fluoride (F) is the inorganic anion of the elemental fluorine (F) atom or of a compound having fluorine. Elemental fluorine is abundant and widely dispersed in the environment in the form of fluorides, with the most abundant form being fluorite (CaF₂), a combination of one Calcium ion (+2) with two Fluorine (-) ions. Fluoride by itself has limited commercial value, its main value being as a source of fluoride in chemical manufacturing. The alkaline nature of fluorite limits its solubility, and, as a result, naturally occurring concentrations of the element in groundwater, fresh, and saltwater sources are low in most areas of the country.

At high concentrations, fluoride (4mg/l or greater) can cause skeletal fluorosis, a bone disease that, in advanced stages, can cause pain or damage to bones and joints.

Fluoride is a mineral found in bones and teeth, and it is used in a common dentistry practice to strengthen tooth enamel. Fluoride, because of its' beneficial properties for preventing tooth decay, is

added to many public drinking water supplies via the Fluoridation treatment processes. Fluoride is also included with many over-the-counter medications, including toothpaste, mouth rinses, and diet supplements, for the same reason.

Elemental fluorine (F) is listed on the Periodic Table of the Elements between oxygen and neon with an atomic number of 9. The Periodic Table organizes the 118 known chemical elements based on their atomic number and the number of protons (+ charge) in the atom's nucleus. The attractive power (electronegativity) of fluorine for carbon is extremely high, and the carbon-fluorine (CF) bond is one of the strongest single bonds in chemistry. The large CF molecules, also identified as covalent bonds, create a three-dimensional structure of atoms bonded together by covalent bonds. The role of fluorine in organic chemistry and PFAS production is discussed later in the course.

Carbon is essential to support life and is the basic element of organic chemistry, all biomolecules have Carbon included in the molecule.

Fluoridation is the treatment process used to add fluoride to drinking water. Commercial fluoride compounds used in the fluoridation processes include sodium fluoride, sodium fluorosilicate (also known as sodium silicofluoride), and fluorosilicic acid (also called hydrofluorosilicic acid). A chemical feed solution is injected into the water system at a point where it can be metered, adequately mixed, and protected with anti-siphon devices. Systems are designed to deliver the optimum fluoride ion concentration as determined by the US Department of Health and Human Services. The recommended fluoride concentration in drinking water is 0.7 mg/l (ppm).

Currently, over 210 million people across the US benefit from access to fluoridated water. The US Public Health Services (PHS) recommends the addition of fluoride to drinking water to prevent tooth decay and reduce the risk of dental fluorosis. Widespread community water fluoridation prevents cavities, and the Center for Disease Control (CDC) considers fluoridation of drinking water one of the greatest achievements in public health protection in the 20th century.

PFAS

Fluorocarbons are used in industry to create polymers, and PFAS were specifically developed to serve as commercial polymers that can be combined with other materials. Nylons, polyethylene, polyesters, PVC, and epoxy are examples of other commercial polymers developed to provide synthetic fibers for:

- textile manufacturing
- structural applications to replace more conventional and heavier materials,
- healthcare-primary medical devices,
- kitchenware-lightweight but sturdy containers,
- toys,
- personal protective equipment, automotive parts,

- and a host of other products.

Biological polymers are also the building blocks for living organisms. Proteins, cellulose and nucleic acids are all created when repeating chains of carbon-based units, critical to supporting cellular growth, combined to form tissue.

Fluorochemicals had their origins in the national effort to build an atomic bomb during WWII when scientists for the Manhattan Project developed safe processes for bonding carbon to fluorine. The derived CF bonds were used in the uranium enrichment process to produce Uranium hexafluoride (UF₆). This chemical is a volatile solid that, when allowed to react with water, releases corrosive hydrofluoric acid. The generated hydrofluoric acid, in turn, interacts with milled uranium ore and after going through a variety of extraction processes, enriched uranium for use in an atomic bomb is produced.

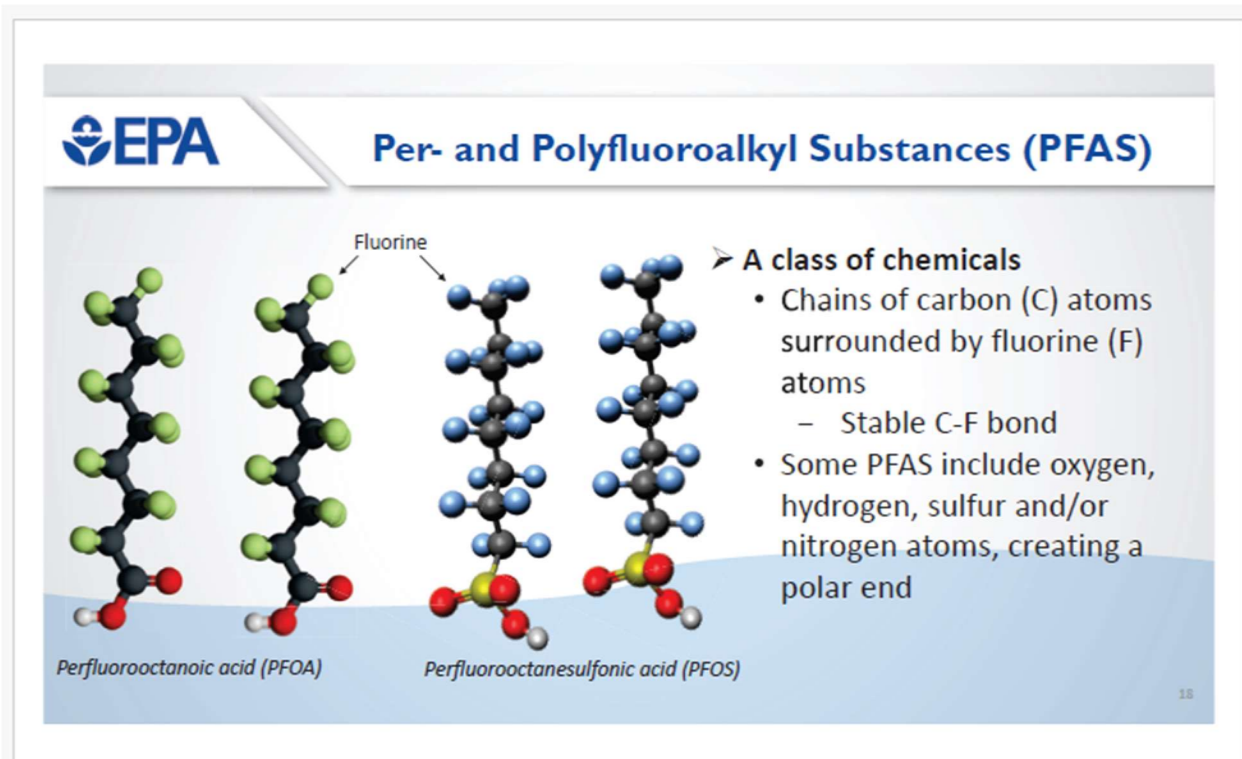


Figure 1 PFAS Explained: EPA

Half-life is the time required for a substance to reduce to half its initial value; for example, the half-life for any given PFAS contaminant is the time it takes for the concentration of the specific PFAS in a body (water, tissue, soil, etc.) to decrease by half.

Because these elements have high chemical stability due to the strong CF bond and are not expected to degrade under normal environmental conditions, they have fairly long half-lives. PFOS and PFOA have apparent half-lives of 41 and 92 years, respectively, when in surface water. Their estimated half-life in humans is also long, ranging from 2 to 8 years.

Elements, because they cannot be divided into smaller parts using normal chemical processes, are the basic building blocks of chemistry. Elemental atoms all include the following basic components:

- (1) protons, the positively (+) charged particles within the nucleus,
- (2) electrons, the negatively (-) charged particles orbiting around the nucleus and
- (3) neutrons, with no electric charge.

The atomic number of an element is the total number of protons associated with the element. Fluorine has 9 protons in its nucleus and 9 electrons that orbit around the nucleus. All available electrons, called valence electrons, found in the outermost orbit are available to be shared among other atoms; Fluorine's high number of valence electrons allows for the bonding of other molecules, crystals, and other structures to create stable, long-chain molecular materials such as plastic polymers.

Electron sharing, i.e., bonding, occurs in many different forms:

- Covalent – electrons are shared between two atoms, like to like or +: + or -: -
 - Hydrogen gas (H_2) is an example of a covalent bond created by the electron sharing between two hydrogen (H^1) atoms, each with 1 valence electron.
- Ionic-ionic bonds are created when an oppositely charged electron is donated or accepted by another oppositely charged electron (+/-).
 - Salt (NaCl), for example, is created when the positively charged sodium (Na^+) atom donates an electron to the negatively charged chloride (Cl^-) atom.
- Metallic- When negatively charged electrons can move freely among positively charged metal ions, metallic bonds form. The charge is spread over larger distances than with covalent or ionic bonds.
 - Zinc and copper metals are examples of metallic bonds that can carry charges over long distances or times.
- Hydrogen – Hydrogen bonds are unique in that although the bonds are weaker than covalent or ionic bonds, they play a critical role in deciding the properties of all matter.
 - Water (H_2O) is the weak bond created when one oxygen (+) and two hydrogen atoms (-) bond together. The hydroxide (OH)ion readily reacts with other positive ions.

The four most important atomic chemistry elements are:

1. Carbon, C+
2. Hydrogen, H-
3. Nitrogen, N+
4. Oxygen, O₋

As previously mentioned, Fluorine has 9 valence electrons, and the number of valence electrons associated with an element is a crucial property in the creation of chemical covalent and ionic bonds and bond properties. Fluorine's high valence number allows promiscuous atomic behavior, and it will interact with other chemical elements to create different bonds.

20th-century chemical technology was able to exploit this behavior to bond fluorine atoms with many long-chain alkyl (+charged) and acidic (- charged) groups used in the manufacturing of different PFAS chemicals. Organic molecules all contain one or more carbon (C) atoms.

- Alkyl groups are chemically created organic molecules that serve as electron (-) provider substitutes used to create new bonding arrangements between atoms and molecules. Methyl, ethyl, propyl, and butyl are common alkyl groups. Alkyl groups are often combined with other elements, creating a wide variety of compounds used in pharmaceuticals, disinfectants, and antiseptics.
- Acidic groups are chemically created organic molecules. Carboxylic acid groups typically present in vinegar and citric acid.
- Carbon-Fluoride bonds will not dissociate under normal conditions. They are highly persistent in the environment. They are used in the production of solvents; CF₄ and their derivatives are used in the production of polymers.
- PFAS compounds are highly stable and do not break down when passing through the environment. They are highly resistant to degradation and visual confirmation of PFAS.
- PFAS bonds also lack the ability to undergo a color change.

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Acidic groups play an essential role in biological processes and, because of their role, hold the potential for certain properties to affect human and animal life. PFAS are one such group with a high potential to adversely affect life.

Organofluoride bonds are the chemical joining of carbon and fluorine atoms to create new molecules. **The bonding of organofluorides to alkyl or acidic groups is the fundamental chemistry process used to create PFAS.** Because many of the manufacturing processes used to create PFAS are proprietary and, oftentimes, trade secrets, performing an outside analysis of their chemistry is difficult to do without the cooperation of the manufacturer.

We earlier reviewed the atomic properties of fluorine elements and their ability to provide or donate electrons to other elements. The fluorine carbon bond is the basic building block common to all